

1 Introduction

1.1 Rovibrational motion in diatomic molecules

The motion of the electrons to be much faster than the motion of the nuclei because the mass of a proton is about 2000 times greater than the mass of an electron. Therefore, in the Born-Oppenheimer approximation we consider the nuclei to be stationary points, while the electrons are moving around the nuclei. In the case of a diatomic molecule, we would have two stationary nuclei.

The relative motion of two nuclei can be described in terms of the motion of a fictitious particle with mass μ moving in an effective potential V_{eff} , thus giving a 3 dimensional problem. This 3 dimensional Hamiltonian can be written in spherical coordinates as,

$$\hat{H} = \frac{\mathbf{p}^2}{2\mu} + V(r) = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\mathbf{L}^2}{2\mu r^2} + V(r) \quad (1)$$

where \mathbf{L}^2 is the angular momentum operator that is defined as,

$$\mathbf{L}^2 = -\frac{\hbar^2}{\sin^2 \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \phi^2} \right). \quad (2)$$

One method for solving this equation is by considering that the full wavefunction $\Psi(r, \theta, \phi)$ can be written as a product of a radial function $R(r)$ and an angular function $Y(\theta, \phi)$. Plugging this into the Schrödinger equation with the Hamiltonian described above gives us,

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\mathbf{L}^2}{2\mu r^2} + V(r) \right] R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi) \quad (3)$$

We know from solving the hydrogen atom that the angular function $Y(\theta, \phi)$ is an eigenstate of \mathbf{L}^2 .

$$\mathbf{L}^2 Y(\theta, \phi) = \hbar^2 l(l+1) Y(\theta, \phi) \quad (4)$$

Using this fact and seeing that $Y(\theta, \phi)$ can be cancelled out lets us write the Schrödinger equation as,

$$-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r R(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} R(r) + V(r) R(r) = ER(r) \quad (5)$$

Multiplying both sides of the equation by r gives,

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} r R(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} r R(r) + V(r) r R(r) = E r R(r) \quad (6)$$

which suggests introducing a modified radial function $u(r)$ such that

$$R(r) = \frac{u(r)}{r} \quad (7)$$

so that we end up with what looks like a one dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} u(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} u(r) + V(r) u(r) = E u(r) \quad (8)$$

where the effective potential V_{eff} described in the beginning is,

$$V_{eff} = \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) \quad (9)$$

$V(r)$ is a potential energy that described the interaction between the two nuclei. The goal of this project is to numerically compute the energies of any diatomic molecule of our choosing using a basis set method. $V(r)$ can be generated using any computational chemistry software package, which leads to us choosing a basis set to carry out the calculations.

1.2 Particle in a box basis

Using the particle in a box eigenfunctions as our basis, we start by defining,

$$|\phi\rangle = \sum_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad (10)$$

Since our problem consists of two atoms at some points r_1 and r_2 , separated by some distance r , we can incorporate this information into our basis definition by defining $x = r - r_1$ and $a = r_2 - r_1$ (figure below). Therefore, $|\phi\rangle$ is defined as,

$$|\phi\rangle = \sum_n \sqrt{\frac{2}{r_2 - r_1}} \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) \quad (11)$$

Since the set of particle in a box eigenfunctions form an orthonormal set, the overlap matrix elements would simply evaluate to kronecker deltas, i.e. $S_{ij} = \delta_{ij}$. Elements of the Hamiltonian matrix are computed as,

$$\begin{aligned}\langle \phi_m | \hat{H} | \phi_n \rangle &= \langle \phi_m | \hat{T} + \hat{V} | \phi_n \rangle \\ &= \langle \phi_m | \hat{T} | \phi_n \rangle + \langle \phi_m | \hat{V} | \phi_n \rangle\end{aligned}\tag{12}$$

The Hamiltonian for our system in atomic units is defined as,

$$\hat{H} = \hat{T} + \hat{V} = \frac{-1}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2\mu r^2} + V(r)\tag{13}$$

The matrix elements of the kinetic energy are:

$$\begin{aligned}\langle \phi_m | \hat{T} | \phi_n \rangle &= \int_{r_1}^{r_2} \phi_m(r) \hat{T} \phi_n(r) dr \\ &= \int_{r_1}^{r_2} \sqrt{\frac{2}{r_2 - r_1}} \sin\left(\frac{m\pi(r - r_1)}{r_2 - r_1}\right) \hat{T} \sqrt{\frac{2}{r_2 - r_1}} \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) dr \\ &= \int_{r_1}^{r_2} \frac{2}{r_2 - r_1} \sin\left(\frac{m\pi(r - r_1)}{r_2 - r_1}\right) \left(\frac{-1}{2\mu} \frac{d^2}{dr^2}\right) \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) dr\end{aligned}\tag{14}$$

The inner derivative is trivial.

$$\begin{aligned}\frac{d^2}{dr^2} \left(\sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) \right) &= \frac{d}{dr} \left(\frac{n\pi}{r_2 - r_1} \cos\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) \right) \\ &= \frac{-(n\pi)^2}{(r_2 - r_1)^2} \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right)\end{aligned}\tag{15}$$

Therefore, the kinetic energy in matrix form is written as,

$$\begin{aligned}\langle \phi_m | \hat{T} | \phi_n \rangle &= \frac{(n\pi)^2}{2\mu(r_2 - r_1)^2} \int_{r_1}^{r_2} \frac{2}{r_2 - r_1} \sin\left(\frac{m\pi(r - r_1)}{r_2 - r_1}\right) \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) dr \\ &= \frac{(n\pi)^2}{2\mu(r_2 - r_1)^2} \delta_{mn}\end{aligned}\tag{16}$$

The matrix elements of the potential energy are:

$$\begin{aligned}
\langle \phi_m | \hat{V} | \phi_n \rangle &= \int_{r_1}^{r_2} \phi_m(r) \hat{V} \phi_n(r) dr \\
&= \int_{r_1}^{r_2} \sqrt{\frac{2}{r_2 - r_1}} \sin\left(\frac{m\pi(r - r_1)}{r_2 - r_1}\right) \hat{V} \sqrt{\frac{2}{r_2 - r_1}} \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) dr \\
&= \frac{2}{r_2 - r_1} \int_{r_1}^{r_2} \left(\frac{l(l+1)}{2\mu r^2} + V(r) \right) \sin\left(\frac{m\pi(r - r_1)}{r_2 - r_1}\right) \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) dr
\end{aligned} \tag{17}$$

Eigenvalues are first found by solving the secular equation,

$$|\mathbf{H} - E\mathbf{I}| = 0 \tag{18}$$

for E, which is an N order polynomial where N is determined by the user. And the eigenvectors are found by solving the eigenvalue equation,

$$(\mathbf{H} - E\mathbf{I}) |a_i\rangle = |0\rangle \tag{19}$$

for $|a_i\rangle$ where $|0\rangle$ is a vector of zeros. The eigenvector for each eigenvalue contains the expansion coefficients c_n for the expansion of an eigenstate in terms of the basis functions. However, the program returns the eigenvectors as a matrix where the ith column represents the ith eigenvector. Therefore, the set of eigenvectors will be denoted as a matrix a_{mn}

$$|\phi_n\rangle = \sum_{m=1}^N a_{mn} \sin\left(\frac{n\pi(r - r_1)}{r_2 - r_1}\right) \tag{20}$$

the expansion coefficients for the expansion of the eigenstate in terms of the chosen basis states.

2 Results and Discussion